

Bench - Scale Study of Sulfur Dioxide Removal in a Carbon Bed

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CERTIFICATE

Certified that the work presented in this thesis entitled, "Bench-scale Study of SO₂ Removal in a Carbon Bed" by Shri Mukesh Kumar Saxena has been carried out under my supervision and has not been submitted elsewhere for a degree.



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ABSTRACT

In the present work, an activated carbon bed has been used to remove sulfur dioxide from the feed gases that is dust free and contains low concentrations of SO_2 . The feed gas (SO_2 in moist air) was passed through the bed at constant space velocity of 1397 hr^{-1} . Activated carbon bed maintained at 90°C significantly removed SO_2 from the feed gas with SO_2 concentration range (2000-3500 ppm) studied. Operation with 2500 ppm sulfur dioxide in the feed gas gave 52% sulfur dioxide removal. Removal efficiency, however, was observed to decrease progressively when the carbon bed was reused after intermittent water washing and drying. The sulfur dioxide removal capability was found to be improved in the iodine treated carbon bed. Iodine solution in concentration range 50-500 mg/L for treating the carbon bed with a flow rate of 20 ml/min for 30 minutes enhanced the percentage SO_2 removal to 72.54 percent.

1. INTRODUCTION

Sulfur dioxide is emitted from coal-fired power plants, from industrial fuel combustion, sulfuric acid manufacturing, and smelting of ores containing sulfur. It is converted by atmospheric processes to sulfates which interfere with normal breathing patterns, reduce visibility, and contribute to the formation of acid rain. Remedial measures are, therefore, necessary to reduce the emission of sulfur dioxide to a tolerable limit. The most obvious and probably most desirable method of reducing the amount of SO_2 emission is to convert more of it into a usable product.

Regulations for sulfur dioxide emissions are already introduced in many countries. In fact, there has been a significant amount of effort expanded worldwide on the development of processes (1) to remove sulfur from the fuel before it is burned, or (2) to remove SO_2 from the exhaust gases. As regards sulfur dioxide removal from exhaust gases, there are essentially two types of effluent gas treatment problems. The first is the problem of removing low concentrations of SO_2 (<0.5% by volume). The second class of SO_2 effluent gas treatment problems comprises those resulting from the need to remove SO_2 from streams containing relatively high concentrations of SO_2 . For example, a smelter emission gas typically contains SO_2 at a concentration of about 10 percent by volume.

Adsorption is particularly well suited to treating effluent gases with very dilute pollutant levels. The solids

best suited for use as adsorbents are those with large surface/volume ratio. Polar adsorbents such as activated aluminas, silica gel, and molecular sieves have selectivity for polar gases. Such adsorbents also effectively remove water, a polar molecule, and thus in the presence of moisture can become ineffective. Activated carbon, however, is composed largely of neutral atoms of a single species, and tends to adsorb all gases roughly in proportion to their concentration.

The objective of the present investigation is to study the removal of sulfur dioxide in a carbon bed, from effluent gases that is dust free and contains low concentrations of sulfur dioxide. It may be mentioned that activated carbon acts as a catalyst to produce sulfuric acid from sulfur dioxide in presence of oxygen and moisture. If the acid produced is periodically removed and fed to sulfur trioxide absorber, such a process will be suitable for the removal of sulfur dioxide from the sulfuric acid plant tail gas.

2. LITERATURE REVIEW

Sulfur oxides (SO_2) have received major attention for many years in the group of irritant anthropogenic air pollutants. They are widely prevalent and of unquestioned physiological significance at higher concentrations. Because of its being more widespread, the problem of sulfur dioxide removal has been subject of more research than other gas purification processes (Peavy et.al., 1986 and Kohl et.al., 1979). The present chapter focusses on the occurrence, sources of emission, effects and removal of various oxides of sulfur present in the atmosphere.

2.1 Occurrence of Oxides of Sulfur in the Atmosphere

2.1.1 Oxides of Sulfur

The oxides of sulfur present in the atmosphere include six different gaseous compounds - sulfur monoxide (SO), sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfur tetraoxide (SO_4), sulfur sesquioxide (S_2O_3) and sulfur heptoxide (S_2O_7) (Peavy et.al., 1986).

However, sulfur dioxide and sulfur trioxide are of prime importance in the study of air pollution control technology.

2.1.2 Sources of Oxides of Sulfur

The sources of the oxides of sulfur are natural as well as anthropogenic, the latter being of prime importance to an environmental engineer. Among the natural sources of sulfur oxides are volcanic eruptions, forest fires and

conversion of hydrogen sulfide into sulfur dioxide as a result of atmospheric reactions. The burning of fossil fuel contributes more than 80 percent of anthropogenic SO_2 emission. Fuel combustion in stationary sources (primarily electric utilities) and industrial processes are the principal contributors of sulfur oxides from human sources (Peavy et. al., 1986).

However, sulfur dioxide pollution can also result from the refining of petroleum; the smelting of ores containing sulfur; the manufacture of sulfuric acid; and the burning of refuse. Transportation contributes little to the anthropogenic oxides of sulfur in the atmosphere because the sulfur content of gasoline is low (about 0.03 percent by mass) (Starkman et.al., 1975).

Many other sources undoubtedly contributes to local problems of sulfur dioxide pollution, but their total emission is of negligible importance as compared to the sources mentioned above.

2.1.3 Emission of Sulfur Dioxide

Sulfur dioxide (SO_2) is formed from oxidation of sulfur contained in fuel as well as from certain industrial processes that utilize sulfur containing compounds. The combustion of fuels, most of the sulfur is oxidized to sulfur dioxide and sulfur trioxide. About 99% of the total sulfur oxides is emitted as sulfur dioxide and 0.5 to 2% as sulfur trioxide (Stern, 1977).

Flue gases from combustion processes normally contain less than 0.5% sulfur dioxide, depending upon the sulfur content of the fuel. Table 2.1 gives the sulfur dioxide content of combustion gases from several typical fuels (Kohl et.al., 1979).

Table 2.1

Sulfur Dioxide Concentration in Combustion Flue Gases*
(Kohl et.al., 1979)

Fuel	SO ₂ in flue gas (%)
Coal 4% sulfur	0.35
Fuel oil 2% sulfur	0.12
Fuel oil 1% sulfur	0.31
Refinery acid sludge, 40% sulfuric acid	2.00

* The values given above are based upon combustion with approximately 15% excess air.

Coal combustion has traditionally been the largest stationary fuel combustion source. The major source of sulfur dioxide in the chemical industry, however, is the manufacture of sulfuric acid. Exhaust gases from the acid absorption tower are the principal source of sulfur dioxide and acid mist emissions. Table 2.2 gives the range in which the concentration of these pollutants are likely to be present in sulfuric acid plants.

Table 2.2

Concentration of Pollutants in Sulfuric Acid Plant Tail Gases
(Crynes, 1977)

Pollutants	Concentration range (ppmv)	Equivalent H_2SO_4 less (%)
SO_2	2000-4000	2-4
SO_3	0-100	<0.1
H_2SO_4 vapour	250-1000	<1.0
H_2SO_4 mist	10-500	<0.5

2.2 Effect of Sulfur Dioxide on Environment

Sulfur dioxide is a colourless, nonflammable, explosive gas with a suffocating odour. It has a taste threshold of $784 \mu\text{g}/\text{m}^3$ (0.3 ppm) and odour threshold of $1306 \mu\text{g}/\text{m}^3$ (0.5 ppm). Sulfur dioxide is highly soluble in water. At a concentration above 3 ppm, it has a very pungent irritating odour (Peavy et.al., 1986).

Sulfur dioxide being highly soluble in water, the gas tends to be dissolved in the moist layer of the upper respiratory tract where protective mechanisms can minimise the injurious effects. However, in polluted urban air oxides of sulfur being adsorbed on fine particulate matters or as sulfuric acid mist may be inhaled deeply into the respiratory tract and can adversely affect the delicate and less protected tissues of the lungs resulting in development of chronic

respiratory diseases, particularly bronchitis and pulmonary emphysema.

The injury to plant life by sulfur dioxide is observed in the form of clearly marked dead tissues between the veins or on the margins of the leaves (due to acute exposure), brownish red or bleached white areas on the blades of leaves (due to chronic exposure), reduction in the yield of crop etc. The plants are particularly sensitive to sulfur dioxide during intense light, high relative humidity and moderate temperature conditions.

In the atmosphere, the sulfur dioxide is partly converted into sulfur trioxide, sulfuric acid and sulfate salts, as a result of photochemical and catalytic processes (Calvert, 1984). Sulfuric acid aerosols will readily attack building materials, especially these contaminants carbonates such as marble, limestone, roofing plates and mortar. The calcium sulfate formed in this process is washed away, leaving a pitted, discoloured surface. Sulfuric acid mists can also damage cotton, linen, rayon and nylon. Excess exposure to SO_2 accelerates corrosion rates for many metals such as iron, zinc, copper and nickel, especially at relative humidity over 70 percent.

2.3 Control of SO_2 from Effluent Streams

Figure 2.1 gives categorization of sulfur dioxide removal processes. The technical and economic feasibility of an SO_2 removal process depends on the type and the quantity of effluent gases that must be cleaned. Removing the

SO ₂ Removal Processes		SO ₂ Removal Agent	Intermediate Steps	Final Product
SO ₂ Removal Processes	Absorption in Liquids	Alkaline Earths	Lime/Limestone Slurry	None — Calcium Sulfite S.
			Oxidation	Calcium Sulfate
			Alkaline Fly Ash Slurry	None — Sludge
			Magnesia Slurry	Thermal Regeneration — Sulfur Dioxide
		Alkali Metals	Sodium Hydroxide/Carbonate/Sulfide	None — Sodium Sulfite
				Oxidation — Sodium Sulfate
				Double Alkali — Calcium Sulfite
				Thermal Regeneration/Crystallization — Sulfur Dioxide
			Sodium Carbonate (Spray Dryer)	None — Sodium Sulfite
				Reduction/Regeneration — Sulfur
			Sodium Citrate/Phosphate/Acetate	Double Alkali — Calcium Sulfite
				Reduction — Sulfur
	Sorption by Solids	Ammonia Compounds	Ammonium Hydroxide/Sulfite	Thermal Regeneration — Sulfur Dioxide
				Oxidation — Ammonium Sulfate
				Double Alkali — Calcium Sulfite
				Auto-Oxidation — Ammonium Sulfate/
		Reaction	Limestone	None — Calcium Salts
			Nahcolite	None — Sodium Salts
			Metal Oxides	Reduction — Sulfur Dioxide
			Alkalized Alumina	Reduction — H ₂ S (or Sulfur)
		Adsorption	Carbon	Oxidation-Reduction — Sulfur Dioxide
				Oxidation-Water Wash — Sulfuric Acid
			Non Reactive Adsorbents	Thermal Regeneration — Sulfur Dioxide
	Gas Phase Conversion	Oxidation	Oxygen	Oxidation-Absorption — Sulfuric Acid
		Reduction	Carbon	Condensation — Sulfur
			Reducing Gas	Catalysis — Sulfur

Fig. 2.1. Categorization of sulfur dioxide removal processes (adapted from Kohl et.al., 1979).

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sulfur from the fuel or removing SO_2 from the exhaust gases are the two basic approaches to SO_2 emission control.

2.3.1 Sulfur Dioxide Control from Power Plant Flue Gas

Four possible methods or alternatives may be used to reduce sulfur dioxide emissions from fossil-fuel combustion. These potential method include (Wark et.al., 1981):

- A. Change to low sulfur fuel
 - 1. Natural gas
 - 2. Liquefied natural gas
 - 3. Low sulfur oil
 - 4. Low sulfur coal.
- B. Use desulfurized coal and oil.
- C. Use flue gas desulfurization (FGD) system.
- D. Tall stacks emission of SO_2 remaining after FGD (for meeting ambient standard).

Flue gas desulfurization is presently the most commercially used technology to comply with SO_2 requirement (Wark et.al., 1981).

Power plant flue gas generally contain low concentrations of SO_2 (<0.5% by volume), but emitted at tremendous volumetric flow rates, and in many respect, the more difficult problem than that of SO_2 removal from smelting and other industrial operations with streams containing relatively high concentrations of SO_2 at low flow rates.

2.3.2 Sulfur Dioxide Removal from Sulfuric Acid Tail Gas

The methods or alternatives that may be used to reduce sulfur dioxide emission from sulfuric acid plants include (Crynes, 1977):

1. Absorption of SO_2 in liquid absorbents.
2. Sulfur dioxide removal by adsorption.

Absorption of SO_2 in Liquid Absorbent: Two processes that have been commonly applied to sulfuric acid plants in this category are sodium or potassium sulfite process (Johnstons, 1940) and ammonia scrubbing process (King, 1937). Both the above mentioned processes are absorption-regeneration type. The main problem in absorption-regeneration process is that a portion of active absorbent reacts to form sulfate, which cannot be regenerated. The other disadvantage of almost all absorption-regeneration processes is the heat requirement of the regeneration process. Tail gas from sulfuric acid plant is normally available only at atmospheric pressure or slightly above it, and with a sulfuric dioxide content of between 2000 and 4000 ppm the partial pressure available is very low. This means high circulation rates between the absorption system and regeneration system and, particularly if the temperature difference between the system is high, a considerable loss of energy as sensible heat or considerable capital expenditures in heat exchangers.

Sulfur Dioxide Removal by Adsorption: Adsorption is a means of concentrating gaseous pollutants, thus facilitating their disposal, their recovery, or their conversion to

Innocuous or valuable product. Sulfur dioxide removal by adsorption on activated solid represents an attractive approach because of ease of regeneration as compared to chemical reaction absorption. The adsorbents commonly used for SO_2 removal are silica gel, ion exchange resins, molecular sieves, activated carbon etc. Although research work had been conducted on SO_2 removal based on ion exchange resin (Shulman et.al., 1960), silica gel (Patrick et.al., 1920) and molecular sieve (Tamboli et.al., 1970) but the adsorption processes for removing SO_2 in presence of moisture which are of commercial significance at this time involve the use of activated carbon.

Activated carbon consists largely of neutral atoms of single species and there are no significant potential gradients to attract and orient polar molecules in preference to nonpolar molecules. It consists of particles of moderately to high pure carbon which has a large surface area per unit volume of solid. Activated carbon is very effective adsorbent even for humid gas stream. For use in fixed bed in air or gas purification, the particles must be so sized that they impose little difference to flow for a given sorption efficiency; the range of 4-20 mesh (sieve size) encompasses the predominant portion of activated carbon for such use (Stern, 1977).

Sulfur dioxide when adsorbed on activated carbon in the presence of excess oxygen, the carbon acts as a catalyst for the oxidation of SO_2 to SO_3 . It has been found that the reaction takes places at an impractically slow rate in absence of water (Kohl et.al., 1979). Activated carbon in presence of

oxygen and moisture serves as a catalyst to produce sulfuric acid. The sulfuric acid is stored in pores of granular activated carbon, then eluted by spraying water on the granules. The water flow down through the carbon bed and is enriched to 10-20% sulfuric acid on its way depending upon the rate of amount of water used (Hartman et.al., 1972).

A variety of metal salts viz. iron, manganese, vanadium and silver salts etc. acts as cocatalyst when added in low concentration to activated carbon, thereby improving SO_2 removal (Johnstone, 1931). The addition of such metal salts, however, contaminates the sulfuric acid produced with metal ions which are difficult to remove. Iodine when added to activated carbon acts as cocatalyst and oxidise sulfur dioxide to sulfuric acid (Schotte, 1976). However, no information is practically available in usual literature about the use of iodine in presence of activated carbon.

Studies by many researchers (Schotte, 1976; Hartman et. al., 1972) have shown that activated carbon serves as good adsorbent for SO_2 removal from sulfuric acid plant tail gases. The carbon adsorption for SO_2 removal may be one preferred method to aid in more sulfuric acid production because of its increased need in fertilizer plants and refineries in our country. However, before such a process could be tested in a under field conditions, detailed study of the process on laboratory-scale is necessary.

3. SCOPE OF THE PRESENT WORK

The present work deals with the study on the removal of sulfur dioxide in a granular activated carbon bed. The feed gas for the carbon bed is a mixture of SO_2 and moist air. It is expected that activated carbon will serve as a catalyst to produce sulfuric acid from sulfur dioxide in presence of oxygen and moisture.

The experimental programmes have been designed to achieve the following objectives for sulfur dioxide removal with granular activated carbon in fixed bed reactor:

1. Generation of breakthrough curves for SO_2 in packed bed of activated carbon under various process conditions like temperature, SO_2 concentration.
2. To study the effectiveness of reused activated carbon bed on SO_2 removal.
3. To study whether the iodine treated activated carbon improves SO_2 removal, as iodine may act as a cocatalyst.

It may be mentioned that the present investigation focusses mainly on SO_2 removal in a carbon bed from effluent gas similar to the sulfuric acid plant tail gas. It is expected that the results of this investigation will be helpful to judge the performance of activated carbon for removing SO_2 under the process conditions stated above.

4. EXPERIMENTAL SET-UP AND PROCEDURE

4.1 Experimental Set-up

The experimental set-up used for conducting experiment has been schematically shown in Figure 4.1. The packed bed system was employed to find out the performance of a reactor system under variable process conditions like inlet SO_2 concentration, temperature etc.

4.1.1 Feed Gas Preparation Section

In the present work, the feed gas was prepared by mixing sulfur dioxide gas and moist air. Air stream was bubbled through water to obtain moist air. Sulfur dioxide was taken from a commercially available sulfur dioxide gas cylinder and constant flow of air was maintained by an air pump (Compress-ovac 70, manufactured by the Unique Industrial Estate, Bombay). The flow of each of two gases were controlled by needle valves and then measured with the help of a separate capillary tube assembly. Then the two gas streams were mixed inside a mixing chamber, which consisted of vertical glass tube of about 27 mm in diameter and 20 cm long, loosely packed with glass wool. The two gas streams enter the mixing chamber at bottom and after mixing leave it at the top.

4.1.2 Preheater and Reactor System

The preheater, which preceded the reactor, was used to raise the temperature of the feed gas. It consisted of vertical glass tube of 27 mm internal diameter and 20 cm long, loosely packed with glass beads and glass wool. It had

port hole at top to measure the temperature with the help of thermometer. The heating coil was wrapped on the outer periphery of the glass tube and it was insulated by putting a 10 mm thick glass wool jacket. The temperature of the feed gas was regulated by heat input by controlling the current through the heating coil with the help of voltage regulator.

The core of the experimental set-up was the reactor where the sulfur dioxide in the feed gas reacts in the carbon bed. It consisted of a vertical glass tube of about 27 mm diameter and 60 cm long, containing a fritted glass plate at bottom. The complete reactor was insulated by 15 mm thick asbestos yarn and glass wool jacket to minimise heat loss. It has two port holes, one at the top and other at the bottom of the side of reactor, for measurement of temperatures in the upper and lower parts of bed. The reactor at the top was provided with a distributor, consisted of a circular plate with holes (dia. - 1 mm) to disperse water fairly uniformly across the top of the bed. The reactor was provided with a valve at bottom to drain the acid produced from the bed.

4.1.3 Water Washing Section

The distilled water was allowed to flow under gravity to the distributor at the top of the reactor.

4.1.4 Sampling Points

The sulfur dioxide concentration of the test gas was measured at the two points - at the inlet of preheater system, and at the outlet of the reactor as shown in Figure 4.1. The gas was sampled with the help of an impinger and

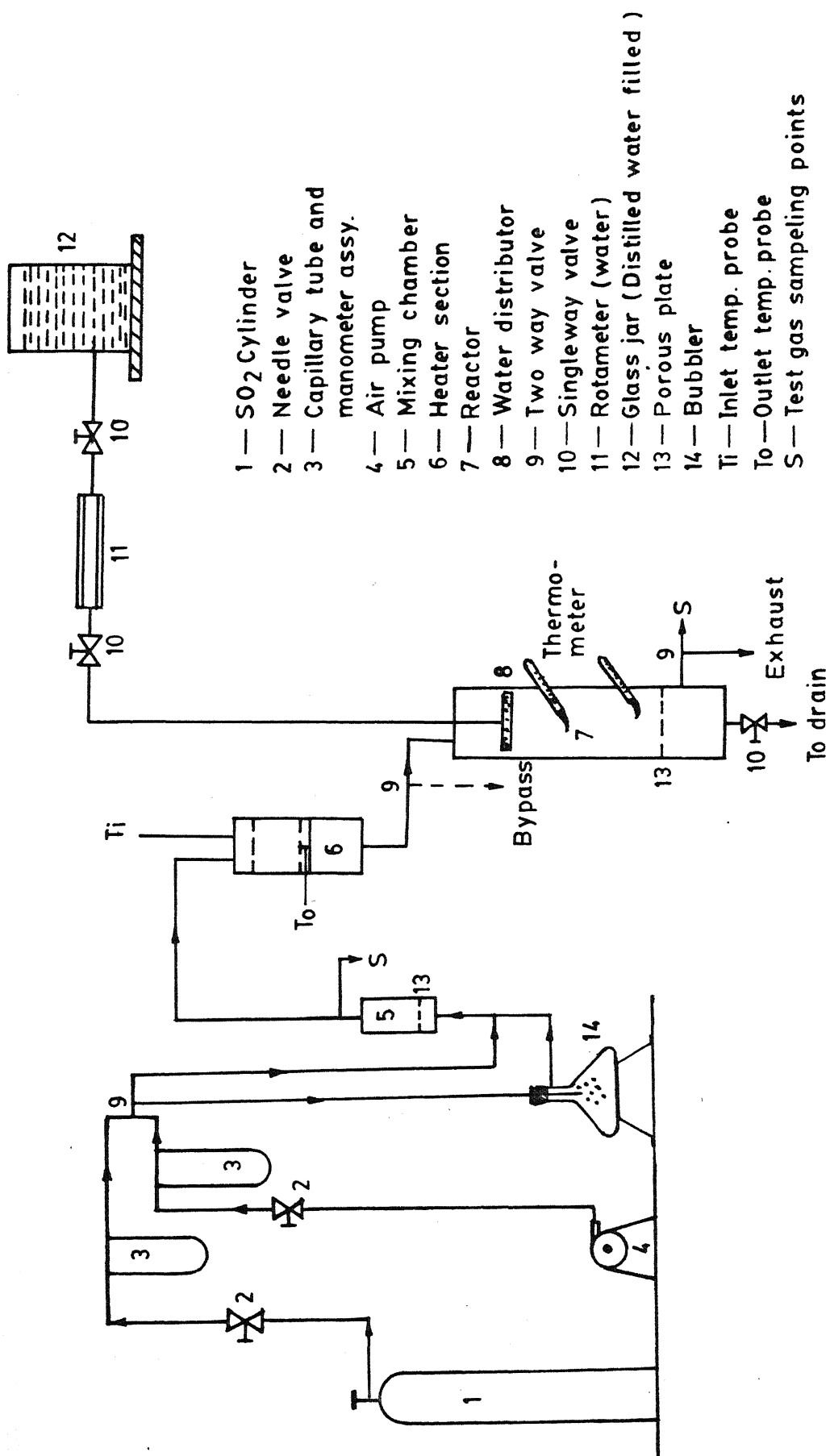


FIG. 4.1 EXPERIMENTAL SETUP

aspirator bottle arrangement. The effluent gas was allowed to cool down to the room temperature before it was sampled.

4.2 Resulting Features

A detailed description of the testing features and operating conditions of present study were given in Tables 4.1 and 4.2 respectively.

Table 4.1
Testing Features

Activated carbon	
Trade name	United Trade Company, Karolbagh, New Delhi
Geometric mean size	1.72 mm
Surface area	300-500 m ² /g
Pore volume	0.1 cc/g
Bulk density	0.45 g/cm ³
Pore radius	10 Å ^o
Diameter of bed	27 mm
Height of bed	150 mm

Table 4.2
Operating Conditions

Composition of feed gas	SO ₂ in moist air
Concentration of SO ₂ in test gas	2000-3500 ppm
Temperature of test gas at inlet of reactor	50-90°C
Flow rate of test gas	2 litre/min
Residence time of test gas	7.158 X 10 ⁻⁴ sec
Space velocity of test gas	1397 hr ⁻¹

4.3 Materials

All the glassware used in the present study was of 'Corning' quality manufactured by Borosil Work Ltd., Bombay. Distilled water and analytical grade reagent were used in the preparation of reagent and all other experimental work.

4.4 Procedure

4.4.1 Preparation of Carbon Bed

For the preparation of carbon bed to activated carbon passing through the sieve with average hole size 2.00 mm and retained on the sieve having average hole size 1.48 mm (thereby giving geometric mean size of 1.72 mm) was used. This activated carbon was packed in reactor to a depth of 15 cm. There is provision for variation of depth up to 40 cm in the reactor. However, depth of activated carbon bed was kept same throughout the experimental study.

4.4.2 Analytical Technique for 'SO₂' Estimation

The concentration of sulfur dioxide in gas mixture was measured by 'sodium tetrachloromercurate method' as given in IS: 5182 (Part-II) - 1969. In this method, sulfur dioxide was absorbed in an absorbing solution (sodium tetrachloromercurate, 0.1 M), where it forms stable dichlorosulfite-mercurate. The amount of sulfur dioxide absorbed, was then estimated by the odour produced, when acid-bleached p-rosaniline hydrochloride and formaldehyde solutions were added to it. The absorbance of the solution, at 560 nm was measured with the help of spectrophotometre 106 (Systronics Pvt. Ltd., New Delhi) and it was matched with the standard plot to get

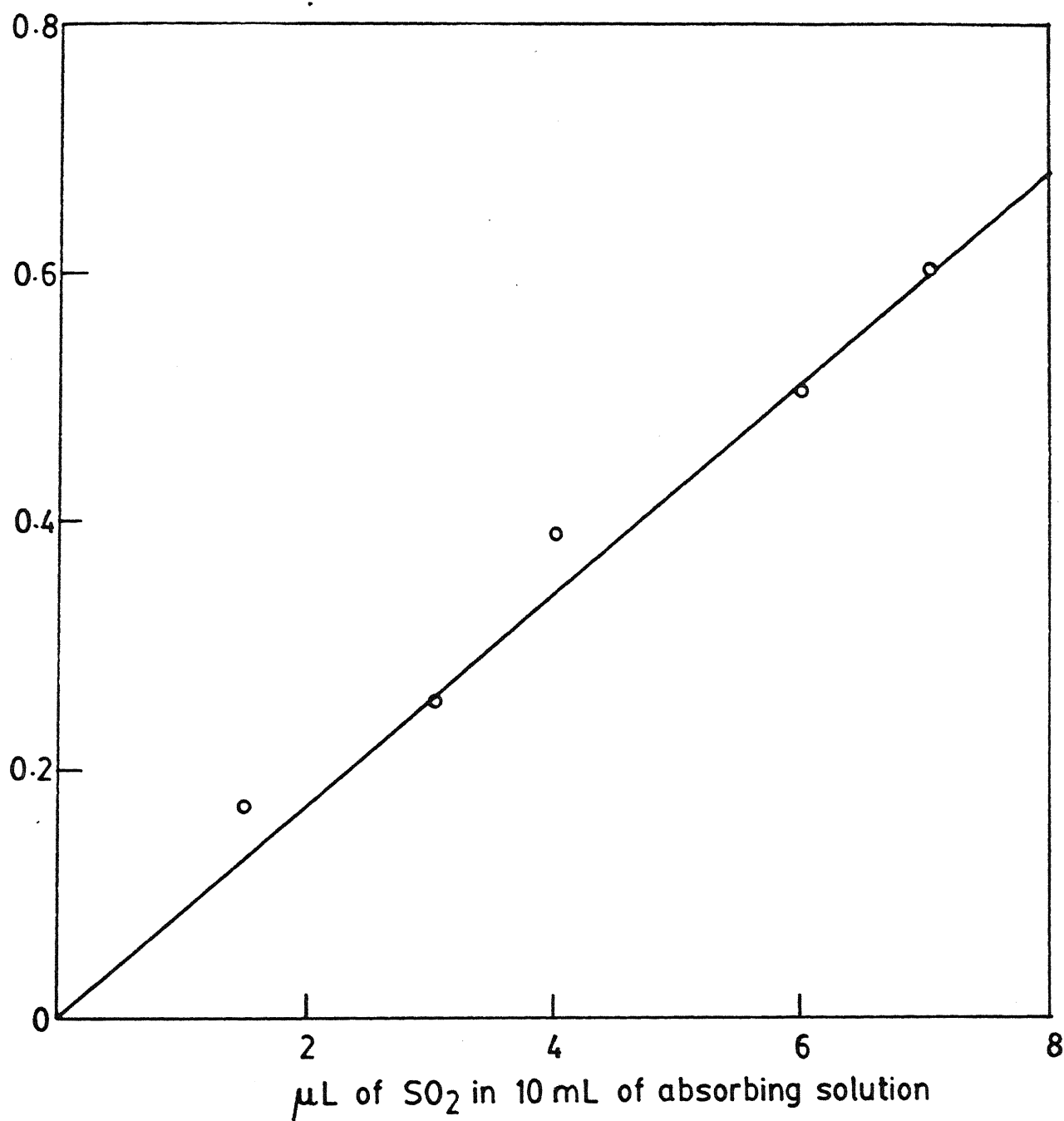


FIG. 4.2 STANDARD PLOT FOR SO_2 BY SODIUM TETRACHLOROMERCURATE METHOD

the amount of sulfur dioxide present in absorbing solution. The concentration of sulfur dioxide in the gas mixture was calculated from this known value of sulfur dioxide present in absorbing solution by the method given in the Appendix A.

A standard plot for sulfur dioxide estimation is shown in Figure 4.2. For higher concentration of sulfur dioxide in gas mixtures sampled, dilution were made before analysis.

4.4.3 Experimental Technique

In the present work a packed bed reactor was used for studying the removal of gaseous ' SO_2 ' in the activated carbon bed.

In the first part of study, fresh activated carbon bed was tested for SO_2 removal under different process variable, namely, SO_2 concentration in the feed gas, temperature of gas stream. Feed gas consisting of mixture of sulfur dioxide and moist air was preheated to obtain the desired reactor inlet temperature. However, prior to testing, the concentration of ' SO_2 ' in the gas mixture and temperature at the inlet of the reactors was ensured to be fairly constant. Then, the gas mixture was passed through the reactor containing activated carbon bed and the gas mixture was sampled for SO_2 concentration at inlet and outlet sampling points, at different time intervals. The space velocity (ratio of gas flow rate to bed volume) was ensured to be fairly constant during the experiment. After, the breakthrough occurred, bed was washed, by passing distilled water through it at constant flow rate (20 ml/min), to remove the acid produced. The wetted activated

carbon bed was dried at $103 \pm 5^{\circ}\text{C}$ in the reactor with dry flow of air through it for about 5-6 hours. A group of experiments were also conducted to test the SO_2 removal capacity of activated carbon bed after periodical removal of acid produced.

In the latter part of study, different concentration of iodine solution were added to fresh activated carbon bed for 30 min at the rate of 20 ml/min. The treated bed was then dried in same manner as mentioned earlier, before being used. A series of experiments were conducted to test the SO_2 removal in the iodine treated activated carbon bed temperature. Inlet SO_2 concentration and space velocity were ensured to be fairly constant during experiments.

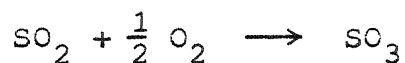
5. RESULTS AND DISCUSSION

The experimental data, calculated results, the effect of variables on percentage SO₂ removal and SO₂ breakthrough curves in an activated carbon bed have been shown in tables and figures of this section.

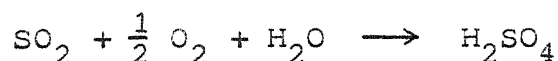
5.1 Effect of Inlet SO₂ Concentration on SO₂ Removal

Experiments were conducted with inlet SO₂ concentration in the range of 2000 to 3500 ppm, at a space velocity of 1397 hr⁻¹ through the carbon bed at a temperature of 90°C. Figure 5.1 shows the fractional outlet/inlet SO₂ concentration (C/Co) versus time curve for various inlet SO₂ concentrations. The amount of SO₂ adsorbed and corresponding percent removal in activated carbon bed, for various concentrations have been reported in Table 5.1. The calculation of these values, at inlet SO₂ concentration of 2500 ppm have been reported in Appendix C.

The behaviour of C/Co versus time curve for SO₂ removal in the carbon bed could be explained from the fact that activated carbon is a good adsorbent and serves as a catalyst to produce sulfuric acid from SO₂ in presence of oxygen and moisture on the basis of following chemical reactions:



These two reactions could be summarised as



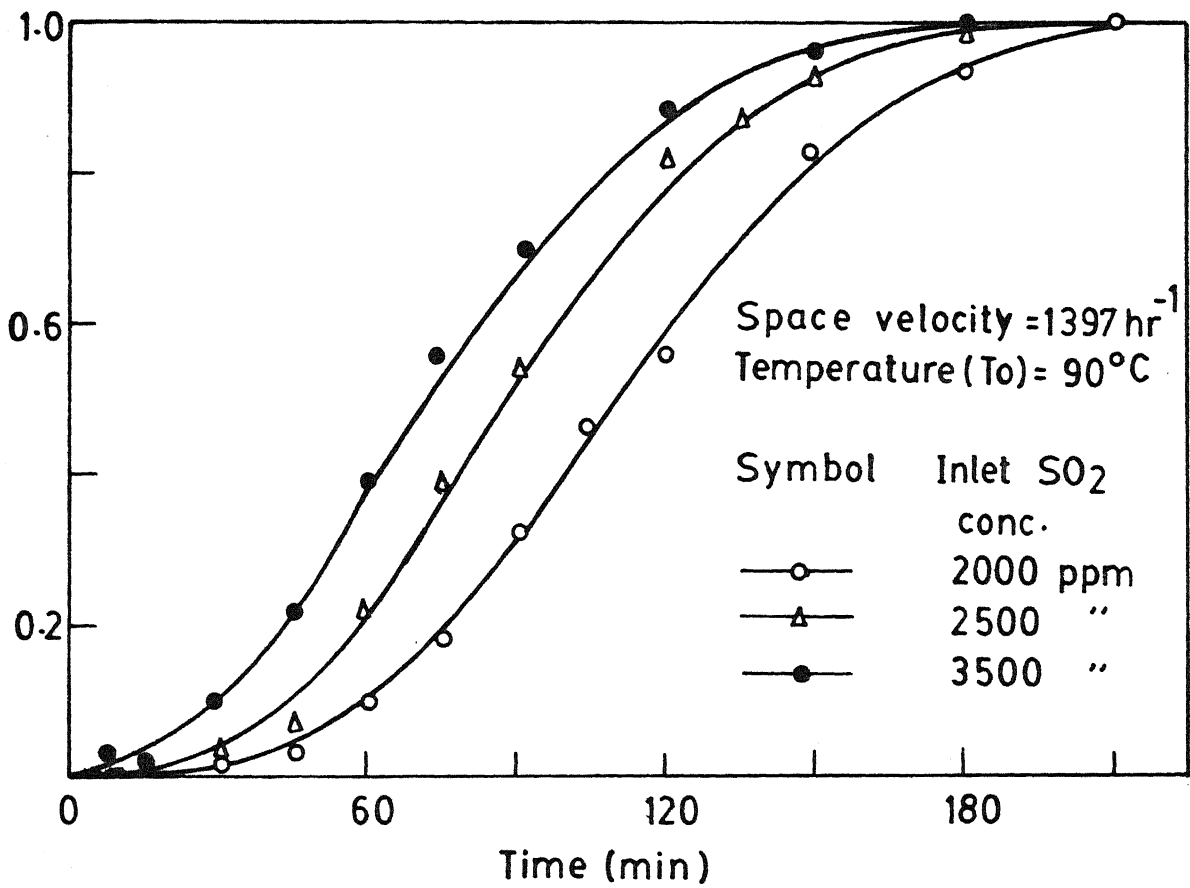


FIG. 5.1 EFFECT OF INLET SO_2 CONCENTRATION ON SO_2 REMOVAL BY ACTIVATED CARBON BED

Table 5.1

Effect of inlet SO_2 Concentration on SO_2 Removal by
Activated Carbon Bed

Temperature (T_o) = 90°C

Space velocity = 1397 hr^{-1}

Co (ppm)	Amount of SO_2 supplied during run in g	Amount of SO_2 adsorbed in bed in g	Percentage SO_2 removal
2000	2.198	1.181	53.73
2500	2.356	1.230	52.21
3500	3.298	1.430	43.50

The calculated value of free energy change (Appendix B) using standard heat of formation and molal entropy value from literature (Weast, 1986), indicate that reactions are feasible.

The early breakthrough at higher concentration might be explained due to rapid formation of sulfur trioxide which quickly covers all the active sites of activated carbon.

5.2 Effect of Temperature on SO_2 Removal

The effect of temperature on SO_2 removal by activated carbon is shown in Figure 5.2. The temperature during the experiments were varied between 50 and 90°C which is the usual temperature range of sulfuric acid plant tail gas. No significant effect of temperature was observed in this range.

5.3 Effectiveness of Reused Activated Carbon Bed on SO_2 Removal

Activated carbon bed was reused after intermittent water

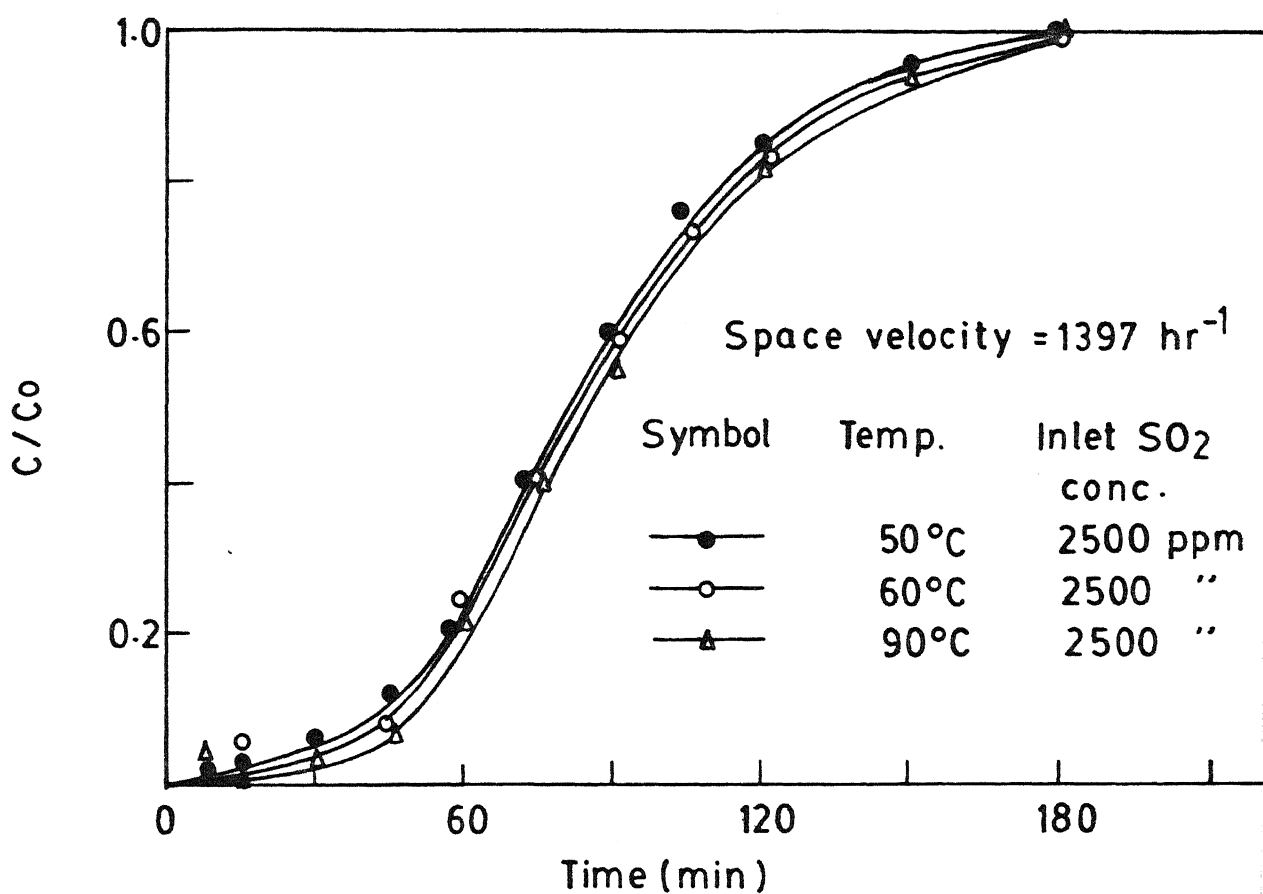


FIG. 5.2 EFFECT OF TEMPERATURE ON SO_2 REMOVAL BY ACTIVATED CARBON BED

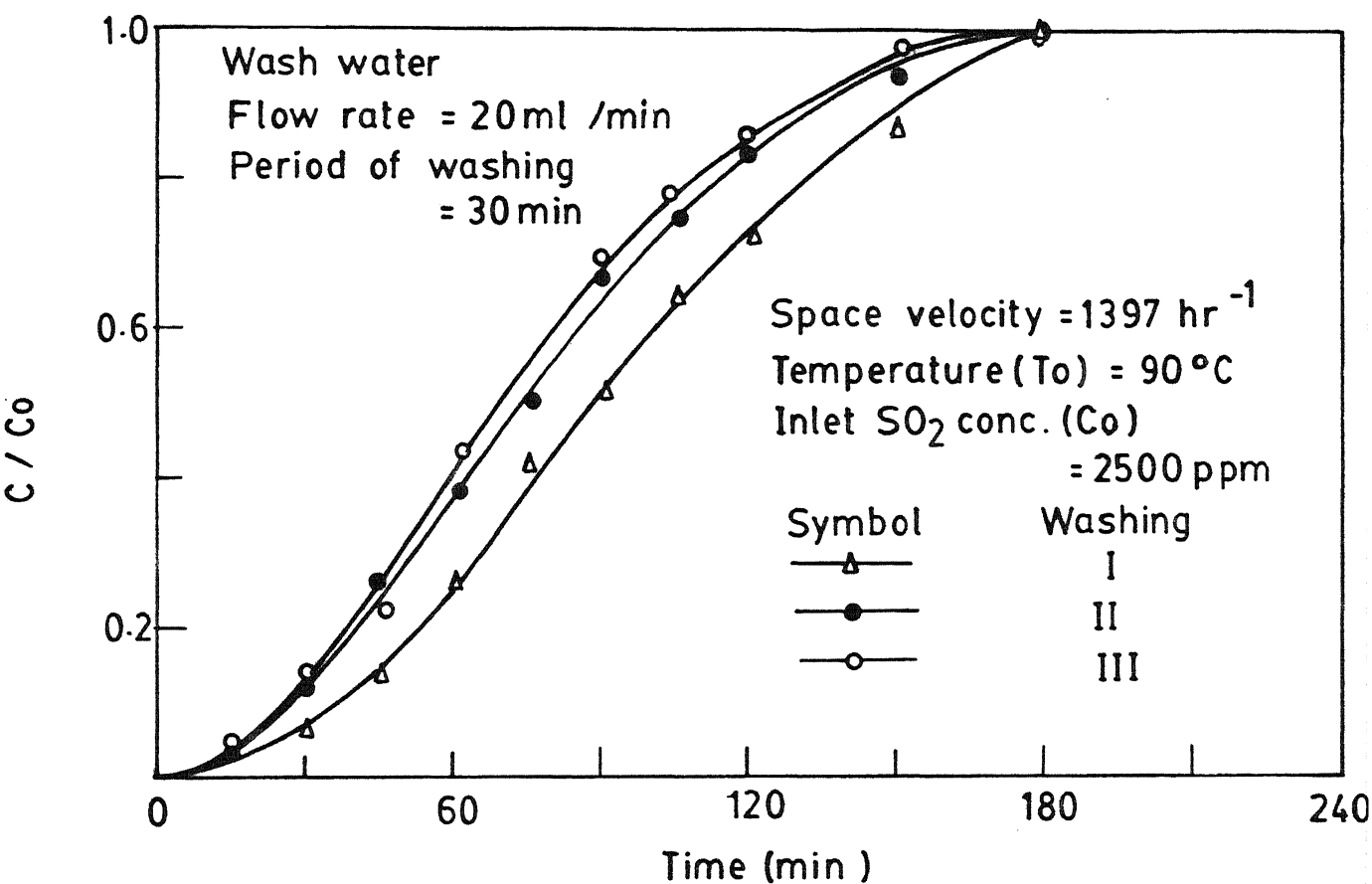


FIG. 5.3 BREAKTHROUGH CURVES FOR REUSED ACTIVATED CARBON BED ON SO₂ REMOVAL

washing and subsequent drying. Breakthrough curves for reused activated carbon bed have been shown in Figure 5.3. The percentage SO_2 removal for the same has been reported in Table 5.2. It was observed that the percentage SO_2 removal decreased progressively with the washing of the carbon bed. However, the said decrease was less dominant after the second washing.

This behaviour could be due to gradual leaching of certain catalytically active metals from carbon. Iron is known to be a catalyst for sulfur dioxide oxidation (Johnstone, 1931). The concentration of iron in acid produced have been reported in Table 5.3. Table 5.3 showed that iron concentration considerably reduced in the produced acid of the each washing. Hence it could be inferred that iron in activated carbon plays an important role in SO_2 removal. This gradual leaching of iron could be responsible for reduced percentage of SO_2 removal.

5.4 Effect of Iodine Treatment of Carbon Bed on SO_2 Removal

It was reported in literature (Johnstone, 1931), that SO_2 removal with activated carbon could be improved by addition of certain metal salts to it. Metal salts when added even at very low concentration contaminated the sulfuric acid produced. However, iodine was found to increase catalytic activity of carbon and would not contaminate the acid produced. Iodine solution in different concentration were added to fresh activated carbon bed. The breakthrough curves for iodine treated activated carbon bed for SO_2 removal have been shown in Figure 5.4. It may be seen from Table 5.4 that percentage SO_2 removal

Table 5.2

Effect of Reused Activated Carbon Bed on SO₂ RemovalTemperature (T_o) = 90°C

Water flow rate = 20 ml/min

Concentration (C_o) = 2500 ppm

Period of washing = 30 min

Space velocity = 1397 hr⁻¹

Cycle of washing	Amount of SO ₂ supplied during run in g	Amount of SO ₂ adsorbed in bed in g	Percentage SO ₂ removal
I	2.35	1.171	49.80
II	2.35	0.9925	42.23
III	2.35	0.945	40.21

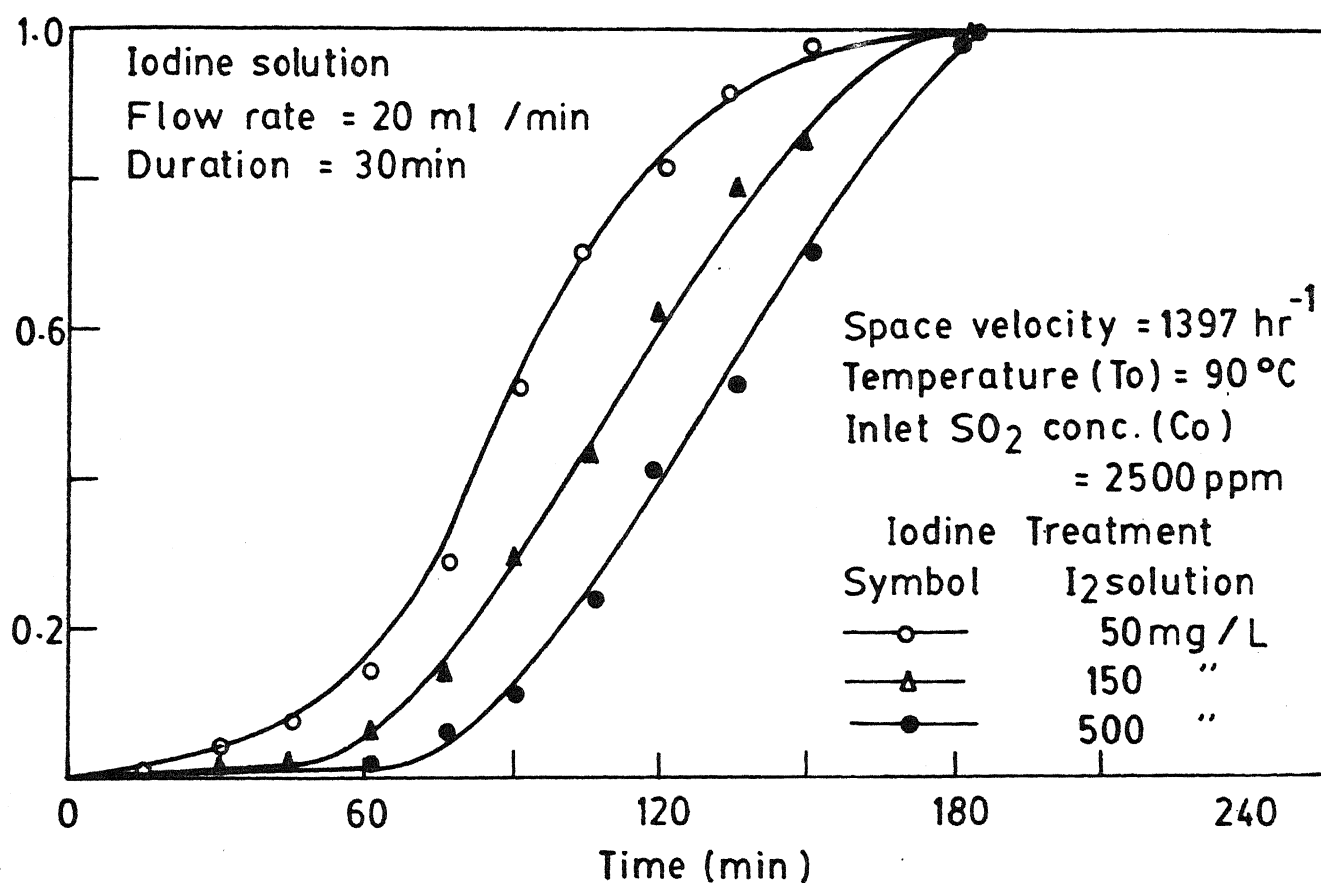
Table 5.3

Concentration of Iron in Sulfuric Acid Produced During Washing of Activated Carbon Bed

Water flow rate = 20 ml/min

Period of washing = 30 min

Time	Iron concentration (mg/L) in acid produced		
	First washing	Second washing	Third washing
2	250	150	42
10	200	80	-
20	-	-	16
30	160	45	8



5. 5.4 BREAKTHROUGH CURVES FOR IODINE TREATED ACTIVATED CARBON BED ON SO_2 REMOVAL

Table 5.4

Effect on Iodine Treatment on Activated Carbon Bed for
SO₂ Removal

Concentration (Co) = 2500 ppm

Temperature (T_o) = 90°CSpace velocity = 1397 hr⁻¹

Iodine solution treatment duration = 30 min

Flow rate = 20 ml/min

Concentration of iodine solution in mg/L	Amount of SO ₂ supplied during run in g	Amount of SO ₂ adsorbed in bed in g	Percentage SO ₂ removal
50	2.35	1.163	49.36
150	2.35	1.416	60.25
500	2.35	1.709	72.54

increased with increased concentration of iodine solutions for treating the activated carbon bed.

This results could be explained on the basis that iodine is strongly adsorbed on activated carbon. This accumulated iodine aids in SO₂ removal possibly according to following reaction:



It may be mentioned here, the calculated value of free energy change (Appendix B), using standard heat of formation and molal entropy values from literature (Weast, 1986), that this reaction is feasible. The reaction will shift more towards

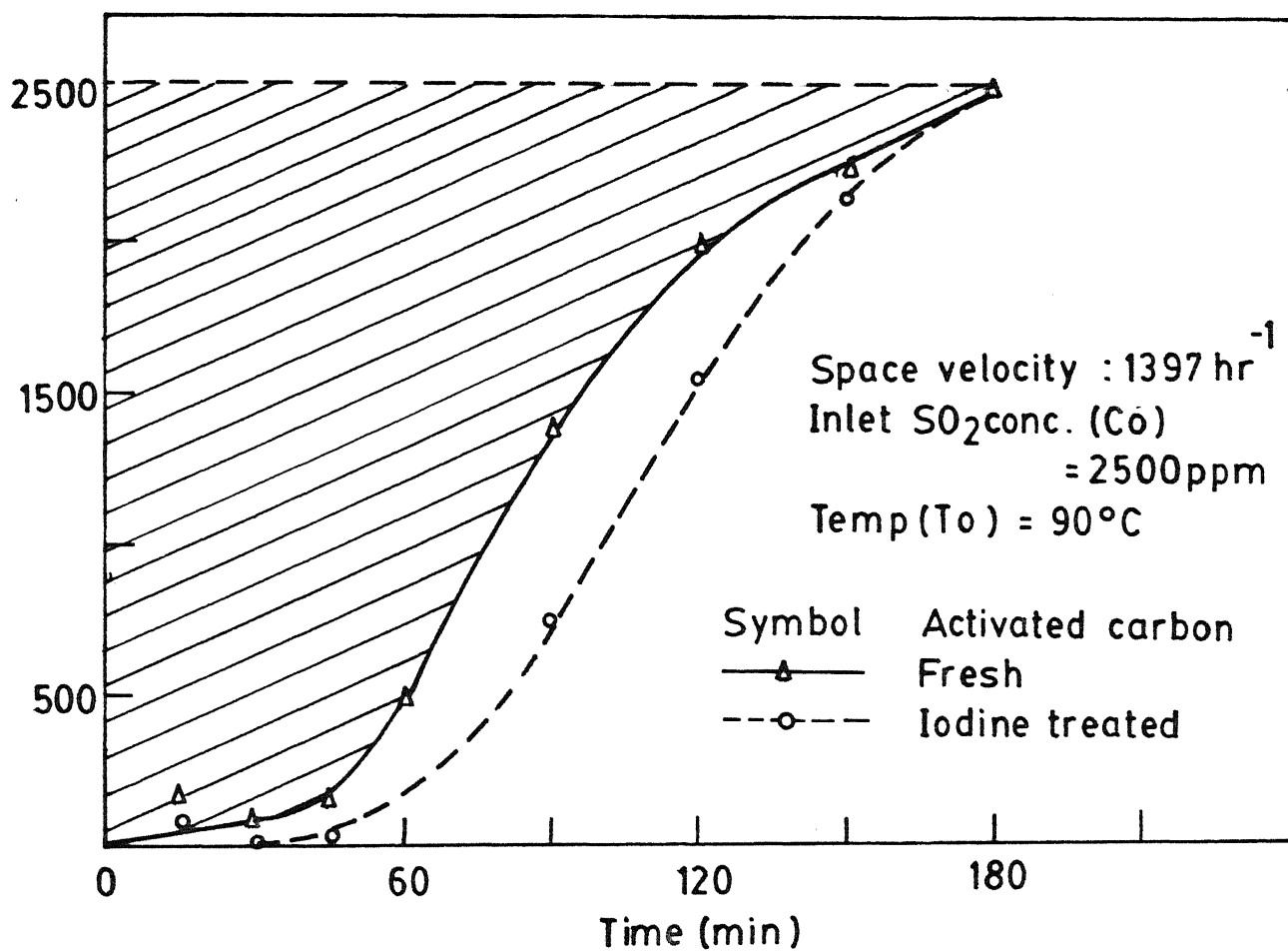


FIG. 5.5 TYPICAL BREAKTHROUGH CURVE FOR SO_2 REMOVAL USING ACTIVATED CARBON BED

right with increased concentration of iodine in the bed. Hence, higher percentage SO_2 removal with increased iodine concentration is expected.

Figure 5.5 shows typical breakthrough curves for fresh and iodine treated activated carbon bed. The strength of sulfuric acid produced was observed to be 0.046 N/600 ml when activated carbon bed was washed with distilled water after breakthrough occurred. The percentage conversion (ratio of actual strength of sulfuric acid produced to theoretical strength of sulfuric acid produced from adsorbed SO_2 in bed) was calculated as 71.25%. However, in case of iodine treated activated carbon bed, strength of sulfuric acid and percentage conversion were found to be 0.065 N/600 ml and 89.04% respectively. The calculation for percentage conversion for fresh activated carbon bed has been shown in Appendix C.

The higher percentage conversion in the case of iodine treated activated carbon bed may be due to the fact that iodine behaved as cocatalyst and aided in SO_2 removal as indicated earlier.

6. CONCLUSIONS

From the foregoing studies, following conclusions may be drawn:

- (1) Activated carbon efficiently removed SO_2 at 90°C with the feed gas SO_2 concentration range (2000-3500 ppm) studied. It was observed that the amount of SO_2 removed by the carbon bed increased with increase in SO_2 partial pressure in the feed gas at that temperature.
- (2) Difference in the SO_2 removal efficiency by the carbon bed maintained in the temperature range $50-90^\circ\text{C}$ at constant space velocity of 1397 hr^{-1} and inlet SO_2 concentration of 2500 ppm was observed to be insignificant.
- (3) The removal efficiency of the carbon bed when reused was observed to decrease progressively with intermittent water washing for removing periodically the acid produced and subsequent drying of the bed. However, significant SO_2 removal occurred even after second washing.
- (4) Iodine treatment on activated carbon bed improved SO_2 removal significantly.
- (5) The percentage conversion of sulfuric acid produced increased with the iodine treatment of activated carbon bed.

7. SUGGESTION FOR FUTURE WORK

The present study indicates that catalytic removal of sulfur dioxide in a carbon bed which will produce sulfuric acid from SO_2 in presence of oxygen and moisture, will be suitable for SO_2 removal from the sulfuric acid plant tail gas. However, further studies, particularly elucidating the mechanism of the reactions involving iodine, are required before testing the utility of such a process in field condition.

In the present work, cocurrent flow conditions was maintained for water and feed gas. Experiments should also be conducted to test the effect of counter current flow condition on ' SO_2 ' removal to check the possibility of using such process as a continuous one. Sulfuric acid removed from the carbon bed can then be fed to the sulfur trioxide absorber.

The space velocity could be varied to test its effects on ' SO_2 ' removal which was not done in the present work. The reaction kinetics of the reaction systems should also be studied.

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APPENDIX A

CALCULATION OF SO_2 CONCENTRATION IN GAS SAMPLE FROM
ABSORBANCE DATA

Let A = Absorbance at 560 nm

V_1 = μl of SO_2 present in 10 ml of absorbing solution
corresponding to absorbance A (from calibration
curve, Figure 4.2)

V_2 = Volume of absorbing solution taken in impinger
for gas sampling, ml

V_3 = Volume of gas sample, ml

n = The dilution number.

$$\begin{aligned}\text{Concentration of } \text{SO}_2 \text{ (ppm)} &= \frac{V_1}{10} \times V_2 \times n \times \frac{1000}{V_3} \\ &= 100 \times n \times \frac{V_1 \times V_2}{V_3}\end{aligned}$$

In the present study, 25 ml of gas was sampled in 20 ml of
absorbing solution in each sampling. Therefore,

$$\text{Concentration of } \text{SO}_2 \text{ in gas sample, ppm} = 80 \times n \times V_1$$

The concentration of SO_2 obtained by above method was within
 $\pm 5\%$ of the calculated values obtained from the flows of SO_2 and
air-through the capillary tube-manometer assembly.

APPENDIX B

THERMODYNAMIC CALCULATIONS FOR THE SULFATION REACTION

The values of the standard enthalpies and entropies of various compounds involved in the reaction are summarised below (Weast, 1986):

Compound	H_{298}° (Kcal./mole)	S_{298}° (cal./mole $^{\circ}\text{K}$)
$\text{SO}_2(\text{g})$	-70.96	59.40
$\text{SO}_3(\text{g})$	-94.45	61.24
$\text{H}_2\text{O}(\text{l})$	-68.32	16.72
H_2SO_4	-216.9	4.1
H_2SO_3	-146.82	-
$\text{O}_2(\text{g})$	0.0	49.003
$\text{I}_2(\text{c})$	0.0	27.9
$\text{HI}(\text{aq})$	-13.37	26.14

From the values given above ΔH_{298}° (the net change in enthalpy) and ΔS_{298}° (the net change in entropy) values were calculated for each of the reactions. To test the feasibility of the reaction, at the temperature of the test gas. ΔG values (the net change in free energy of the reaction) were calculated by the following equations:

$$\Delta G = \Delta H_{298}^{\circ} - T \cdot \Delta S_{298}^{\circ}$$

$$- . . . \quad \text{where } T = \text{Temperature } (^{\circ}\text{K})$$

The calculation of ΔG values is summarised below:



$$\Delta H_{298}^{\circ} = -23.49 \text{ Kcal.}, \quad \Delta S_{298}^{\circ} = -22.68 \text{ cal./}^{\circ}\text{K}$$

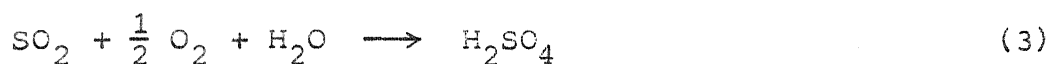
$$\Delta G_{90^{\circ}\text{C}} = -15.25 \text{ Kcal.}$$



$$\Delta H_{298}^{\circ} = -54.22 \text{ Kcal.}, \quad \Delta S_{298}^{\circ} = -73.86 \text{ cal./}^{\circ}\text{K}$$

$$\Delta G_{90^{\circ}\text{C}} = -27.40 \text{ Kcal.}$$

The overall reactions can be summarised as



$$\Delta H_{298}^{\circ} = -77.62 \text{ Kcal.}, \quad \Delta S_{298}^{\circ} = -96.52 \text{ cal./}^{\circ}\text{K}$$

$$\Delta G_{90^{\circ}\text{C}} = -42.58 \text{ Kcal.}$$



$$\Delta H_{298}^{\circ} = -36.84 \text{ Kcal.}, \quad \Delta S_{298}^{\circ} = -64.36 \text{ cal./}^{\circ}\text{K}$$

$$\Delta G_{90^{\circ}\text{C}} = -18.47 \text{ Kcal.}$$

APPENDIX C

CALCULATION FOR PERCENTAGE SULFUR DIOXIDE REMOVAL AND
SULFURIC ACID PERCENTAGE CONVERSION

The following calculations are based on breakthrough curve for inlet 'SO₂ concentration' of 2500 ppm as shown in Figure 5.5.

1. Activated Carbon Bed

The total amount of SO₂ adsorbed during the test run can be calculated by obtaining the area above the recorded breakthrough curve, shown shaded in Figure 5.5. It is known that

$$1 \text{ ppm of SO}_2 = 2617.6 \text{ } \mu\text{g/m}^3 \text{ (at S.T.P.)}$$

$$\text{Volumetric flow rate of gas} = 2 \times 10^{-3} \text{ m}^3/\text{min}$$

$$\begin{aligned} \text{Value of 1 cm square on graph} &= 250 \times 15 \times 2 \times 10^{-3} \times 2617.6 \\ &= 19632 \text{ } \mu\text{g} \end{aligned}$$

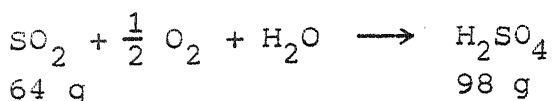
$$\text{Total no. of squares in desired shaded area} = 62.64$$

Hence,

$$\begin{aligned} \text{Total SO}_2 \text{ adsorbed} &= 62.64 \times 19632 \text{ } \mu\text{g} \\ &= 1.23 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Total amount of SO}_2 \text{ supplied during the run} &= 180 \times 2617.6 \times 2500 \times 2 \times 10^{-3} \text{ } \mu\text{g} \\ &= 2.35 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Therefore, percentage SO}_2 \text{ removal} &= \frac{1.23}{2.35} \times 100 \\ &= 52.32\% \end{aligned}$$



64 g of SO_2 will produce 98 g of H_2SO_4

$$\begin{aligned} 1.23 \text{ g of } \text{SO}_2 \text{ adsorbed will produce} &= \frac{98}{64} \times 1.23 \\ &= 1.883 \text{ g} \end{aligned}$$

The following calculation is based on assumption that cent percent conversion of SO_2 adsorbed into sulfuric acid.

49 g of H_2SO_4 dissolve in 1 litre will produce 1 N solution.

$$49 \text{ g in 600 ml will produce} = 1.667 \text{ N}$$

$$1.883 \text{ g in 600 ml will produce} = \frac{1.667}{149} \times 1.883$$

$$\text{Thus theoretical strength of } \text{H}_2\text{SO}_4 = 0.064 \text{ N}$$

Strength of sulfuric acid actually produced

$$= 0.046 \text{ N/600 ml}$$

$$\text{Hence percentage conversion} = \frac{0.046}{0.064} \times 100$$

$$= 71.875\%$$

2. Iodine treated activated carbon bed (for I_2 soln.conc. 150 mg

$$\text{Total } \text{SO}_2 \text{ adsorbed in bed} = 1.416 \text{ g}$$

Theoretical strength of H_2SO_4 (calculated from Fig. 5.5)

$$= 0.073 \text{ N/600 ml}$$

$$\text{Strength of acid produced actually} = 0.065 \text{ N/600 ml}$$

$$\text{Hence percentage conversion} = \frac{0.065}{0.073} \times 100$$

$$= 89.04\%.$$